

Evidence for Long-term Nitrogen Loss from Desert Soil Profiles: A 14.6 ka Record Inferred from Vadose Zone Pore Waters in Southern Nevada

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Abstract

A 14.6kyr chronology of nitrogen losses from the active rooting zone in southern Nevada, USA suggest that nitrogen has not been the limiting factor for plant growth nor is the biotic community capable of utilizing all available nitrogen in these desert soils. Soil water chemistry from corings in the deep vadose (unsaturated) zone was measured to develop a chronology of paleohydrology and nitrogen fluxes from the active rooting zone. The archived chronology is estimated to span 14.6 kyrs based on accumulated chloride in the soil profile. Extremely high levels of nitrogen (as NO_3) dissolved in pore waters were found directly beneath the modern rooting depth. Nitrogen fluxes from the active root zone ranged from 103 to 108 $\text{mg/m}^2/\text{yr}$ and appear stationary in spite of dramatic climate changes. The observed flux is approximately twice the modern atmospheric deposition rate and we postulate that nitrogen fixation by surface microbes and vegetation accounts for the residual flux. The long-term loss of nitrogen from the active rooting zone implies that the biological community may not be limited by the availability of nitrogen, and the loss of nitrogen into the vadose zone must be considered in desert ecosystem productivity studies. This work also confirms previous results implicating root zone nitrogen losses to elevated levels of nitrogen (as nitrate) in desert aquifers.

Nitrogen fluxes and cycling, often cited as a limiting factor in desert biological processes (1) can be inferred from deep vadose (unsaturated) zone profiles under conditions of low moisture content and small rates of liquid water (2, 3). The very low soil moisture fluxes below the active rooting depth allow preservation of pore water chemistries, archiving ground water recharge periods ranging from decadal to millennial (2, 4, 5, 6). In the American Southwest, several workers (4, 6, 7) have shown strong correlation between the Last Glacial Maxima (LGM) and significant periods of ground-water recharge preserved in vadose zone pore water chemistries(6). In each of these studies, the preservation of the climate signatures in the vadose zone relies on 1) the observed small volumetric water contents of the sediments (<10%) which limits the magnitude of solute diffusion within the porous media and 2) the small rates of liquid flux, which limits the dispersion of the solute signature. Most studies of vadose zone archives however rely upon stable isotopes and chloride isotopes in pore waters to infer paleoclimatic information and do not consider nitrogen as an appropriate tracer. Our research indicates that elevated concentrations of nitrogen often observed in pore waters

in arid vadose zones (3, 8, 9, 10, 11) can be used to infer biotic activity, nitrogen loss from desert soils and sources of elevated nitrogen in desert aquifers over millennial time scales. The high concentrations of nitrogen often observed in arid vadose zones (3, 8, 9, 10, 11) implies that its preservation in desert vadose zones can also be used to infer rates of biotic activity and nitrogen loss from desert soils.

A series of shallow and deep borings in Yucca Flat, Nevada (Figure 1) within the southern Basin and Range Province of the western United States were made to assess the rates of ground water recharge and nitrogen fluxes below the active rooting zone. The ground water depth is 460 meters (making it one of the deepest in the continental United States) and the vadose zone consists primarily of alluvial sediments. The surface soils are classified as sandy loams with little soil development, limited aggregation, very low organic carbon content (9) and low water volumetric water contents (8-25%). Caliche or impeding layers were not observed in any of the borings. The present climate of the region is arid, with annual precipitation of 167 mm/yr. Vegetation consists of shallow rooted (~1 meter) Mojave Desert species. Soil cores were mechanically collected every 0.3 m to a depth of 46 m with 7 shallow cores hand augured to a depth of 5 meters within a 50 meter radius of the deep core site to investigate the effects of vegetative islands (12) and surface topography.

Figure 2a shows the observed chloride and nitrate (NO_3 as N) (13) concentrations in pore waters from the deep (46m) borehole, while Figure 2b shows the solute concentrations in the 4 of the 7 adjacent 5-meter corings. Near the land surface, solute concentrations of both species are low, reflecting active flushing by precipitation and plant uptake. Below approximately 1 meter, corresponding to the observed depth of modern rooting, both chloride and nitrate concentrations increase, reaching maxima at 2-3 m below land surface and rapidly decreasing at depths greater than 5-6 m. The chloride profiles are typical of many desert vadose zone profiles and have been attributed to a reduction in downward soil water flux coincident with the Pleistocene/Holocene climate transition (4, 14). Prior to the climatic transition, downward infiltration dominated the vadose zone and enrichment of chloride in these waters was limited. Waters infiltrated during these periods, now found at depth, are characterized by soil water chloride concentrations 10-15 times that found in precipitation and suggest paleofluxes of water from the root zone of 9 mm/yr (15). At the onset of aridity, deep infiltration was significantly reduced and enrichment of chloride in soil waters exiting the root zone became significant. Pore water chloride concentration in waters infiltrating during arid periods can approach seawater concentration (14). The elevated chloride concentrations found directly beneath the root zone suggest a modern water flux of less than 0.1 mm/yr. Alternatively, the chloride concentrations could represent preferential or bypass flow (5, 16). The lack of both significant soil structure and vertical textural variation, combined with the similarity between chloride and nitrate profiles suggests that preferential flow is unlikely in these profiles and therefore chloride profiles can be used to infer fluxes and soil water age (4, 14).

Deuterium and oxygen-18 of pore waters extracted from the 46 m core show a strong evaporation signature near the land surface, while soil waters from deeper in the 46 meter

profile are significantly depleted ($\delta D = -118\text{‰}$, $\delta^{18}\text{O} = -15\text{‰}$) as compared to modern precipitation at the site(14), suggesting that these waters were derived from precipitation under cooler, LGM climates (17). Additional evidence for LGM waters deep in the profile is contained in $^{36}\text{Cl}/\text{Cl}$ ratios of pore waters. Extraction of pore waters from depths of 10.97 and 23.3 meters yielded ratios of 772×10^{-15} and 1050×10^{-15} respectively significantly elevated above modern concentrations in precipitation (18). $^{36}\text{Cl}/\text{Cl}$ chronologies previously developed for the region (19) support a minimum age of the soil water at a depth of 23.3 meters of 10-12kyrs. The concurrence of both isotopic and stable chloride signatures strongly suggests that the vadose zone waters below the active rooting depth represents an archive of water and solute flux beneath the root zone from the present through the Pleistocene/Holocene transition to the LGM.

The coincidence of chloride and nitrate concentrations in all borings is surprising. While chloride originates primarily from atmospheric deposition (as confirmed by Cl/Br ratios in soil waters from adjacent areas (14, 20), nitrogen originates both from deposition and fixation within the soil zone. Chloride/nitrate concentration ratios remain relatively constant at all depths and borings suggesting that nitrate is behaving as a conservative species and negligible loss by organic or inorganic processes occur deep in the vadose zone. The low water contents and oxidizing environment in the very near surface vadose will favor nitrification; once below the root zone, few processes are available to uptake or convert nitrate. The presence of elevated nitrate below the active root zone strongly suggests that nitrogen is not a limiting factor for the desert biota, and some proportion of fixed and deposited nitrogen has been continuously lost from the rooting zone in a manner similar to the conservative chloride tracer.

The archival period for nitrogen in the vadose zone was inferred from chloride accumulation with depth in each of the profiles referenced here. Here we assume that the principle direction of water movement is vertical. On a fine scale, such an assumption is clearly a simplification as surface and subsurface heterogeneity will produce complex flow directions in the vadose zone. However, the relative similarity between the deep and shallow core profiles as well as previous work on vadose archives (14) suggests that, to first order, the flow direction below the active rooting depth is primarily vertical and a chloride mass balance may be used to infer both rates of water flux and soil water age(21). Under this assumption soil water age at each sample depth was calculated as the total mass of chloride stored above the depth divided by the estimated yearly atmospheric chloride deposition rate. Previous workers have suggested that atmospheric chloride deposition has not varied dramatically in this vicinity through the Holocene period (19) and that chloride in these coarse textured soils is a conservative tracer (22). Figures 3a and 3b show the estimated soil water ages verses depth under an assumed constant surface chloride flux of $88 \text{ mg/m}^2/\text{yr}$. At the 46 meter depth, soil water ages are ~12-14 kyr coinciding reasonably well with the LGM and Holocene / Pleistocene transition. Low concentrations deep in the profile imply a period of significant deep infiltration and limited soil water chloride enrichment by surface evapotranspiration. Several proxy climate records are available from the area, which confirm that deep infiltration and significant ground-water recharge was likely during this time (23, 24).

Nitrogen fluxes from the root zone can be calculated at each sample depth from the difference in soil water age between sample intervals and the mass of nitrogen contained in the interval. However, diffusion and the observed modern upward water flux (as inferred from water potential measurements from core samples) make this calculation poorly constrained. Rather, we calculate the average nitrate flux over the entire record in each borehole by dividing the total accumulated nitrogen beneath the root zone by the length of record. Over the entire 46 meters of the deep core (spanning the last 14.6 kyr), the mean nitrate flux is calculated to be 103 mg/m²/yr.

The chloride and nitrate concentrations in the 5-meter cores show some spatial heterogeneity and contain an abbreviated record of 2-8 kyr of chloride and nitrate accumulation. The mean nitrate flux for the shallow core network is 108 mg/m²/yr, similar to the deep core flux in spite of the shorter period of record. The standard deviation of the flux is 42 mg/m²/yr, while the extremes are 59 mg/m²/yr and 172 mg/m²/yr. The large variation is likely due to lateral flow, spatial distribution of vegetation and microtopography differences that provide different recharge regimes and potential variations in the flux at shorter timescales. However, there is no relation between soil water age (as measured in each boring) and the nitrate flux, suggesting spatial heterogeneity in deep water flux rather than biological heterogeneity.

The similarity in calculated fluxes over 14.6 kyr (46 m core) and 2-8 kyr (shallow cores) suggest that long term average nitrate fluxes below the root zone throughout the late Pleistocene and Holocene have remained relatively constant. This is in spite of the significant changes in vegetation well documented in the southern Great Basin at the Pleistocene/Holocene transition. These changes had significant impact on ground water recharge (4, 14) yet appear to have little impact on the loss of soil nitrogen. This conclusion differs from the short (<400 yr) records of nitrogen loss from the African Sahel (3) that display correlation to vegetation/climate records and results from the longer time averaging inherent in our record, in which the high frequency fluctuations in nitrogen flux, would not be discernable.

The contribution of various nitrogen sources over the period of record can only be inferred. Nitrogen released from rock weathering(10) below the rooting depth appears insignificant, as the observed Cl/NO₃ ratios in the pore waters are relatively uniform with depth. Modern atmospheric wet and dry deposition is estimated to be 50-60 mg/m²/yr based upon regional data (25). Nitrogen paleo-deposition records are only available from distant ice cores (26, 27) and lack strong evidence of variations in nitrogen over the last 14 kyr. In the northern Great Basin, enhanced nitrogen deposition was shown (28) to be correlated to proximity to desiccated playas, with measured fluxes of 110-mg/m²/yr 1 km downwind from the playa surface. Several workers(28, 29) speculate that nitrogen fixation on the playa surfaces by algae/lichen crusts. Our study site is located 1.8 km north of Yucca Playa and localized dry deposition may be enhanced over regional estimates.

Net biological sources (fixation) at the soil surface from algae/lichen communities in the northern Mojave have been estimated at ≤10 mg/m²/yr (30) while fixation deeper in

the root zone where rhizosphere processes are also possible. The presence of solely nitrate species in the deep vadose zone suggests that decomposition and oxidation occurs only near the surface as the high salinity deep in the profile will inhibit transformations (31). Finally, the loss of nitrogen does not appear to result from depletion of existing nitrogen pools within the root zone as our observed fluxes do not decline with increasing soil water age.

The above discussion suggests that, while nitrogen is actively lost from the soil pools in the root zone, nitrogen losses downward into the deep vadose zone appear to be balanced by inputs. As a preliminary conclusion, regional atmospheric deposition appears to contribute approximately 49-58% (50-60 mg/m²/yr) of the observed nitrate flux beneath the rooting zone, with the remaining 42-51 % (43-53 mg/m²/yr) of the flux resulting from localized eolian transport and some nitrogen fixation by surface algae and lichen.

The net loss of nitrogen from the rooting zone resulting from the depletion of existing nitrogen pools in the soil zone is not supported from the pore water chemistries deep in the profile. We would expect that this depletion should decrease with time and is not supported by our apparent constant flux. Therefore, the fixation of nitrogen, by terrestrial plants and cyanobacteria, directly from the atmosphere appears to be the likely candidate for the remaining observed flux. Current species, and species recorded (23) at the Pleistocene/ Holocene transition in the area are not efficient nitrogen fixers. The primary candidate for modern as well as past high deposition rates remains fixation by algal-lichen crusts. Leatham (9) conducted laboratory experiments to quantify production rates of cyanobacteria found at the land surface at sites in Yucca Flat. Production rates were highly dependent on moisture contents with an average of 89 mg NO₃-N/m²/day. The bacteria were capable of withstanding periods of drought and were immediately revived with the addition of moisture suggesting that brief periods of soil moisture could easily account for the observed flux from the root zone.

The use of both shallow and deep cores, archiving records of differing length reduces the uncertainties in time-varying advective and diffusive processes in these deep vadose zones. The records suggest that fluxes from the root zone have been relatively stationary throughout the last 14 kyrs, in spite of significant climate and vegetation changes. The data also suggest that the desert vegetation and biota found at the site do not utilize all available nitrogen, but rather some nitrogen is transferred from the root zone into the deep vadose zone, where eventually it will be transported to the ground water. This is consistent with previous work (3) suggesting that elevated NO₃ levels in desert ground waters are the result of nitrogen losses from the root zone. In Yucca Flat, loss of biologically fixed nitrogen appears to be similar in magnitude to nitrogen deposition from precipitation and dry deposition over the last 14 kyrs.

The use of vadose zone solute profiles as proxy paleoclimate/paleo ground-water recharge records has been widely applied in arid and semiarid regions. The extension of these records to include nitrogen implies that much more information about vegetation history, nutrient pools and anomalous nitrate often found in desert aquifers can be

inferred from vadose zone profiles. Data from this study strongly suggests that nitrogen, in itself has not been a limiting factor in biotic productivity. Rather, its availability may be limited by lack of available water and/or leaching from the active root zone during periodic infiltration.

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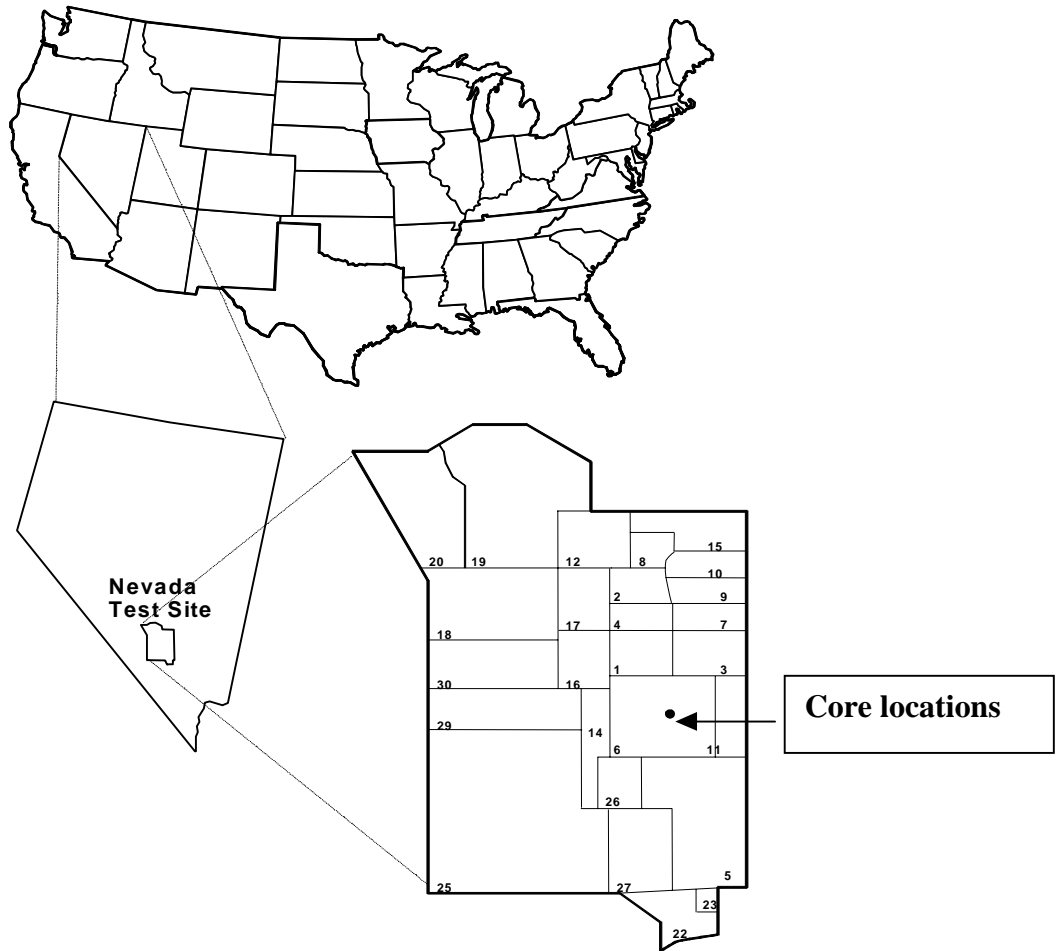


Figure 1
Location of Yucca Flat Study Site, southern Nevada, USA. Yucca Flat is located within the U.S. Dept of Energy’s Nevada Test Site. The study site is located at an elevation of 1199m in a flat lying basin surrounded by the Half-pint Mts. to the east and Syncline Ridge and Mine Mts. to the west. The upper 50m of the vadose zone consists of coarse textured alluvium derived from Paleozoic carbonate and Mesozoic volcanic rocks.

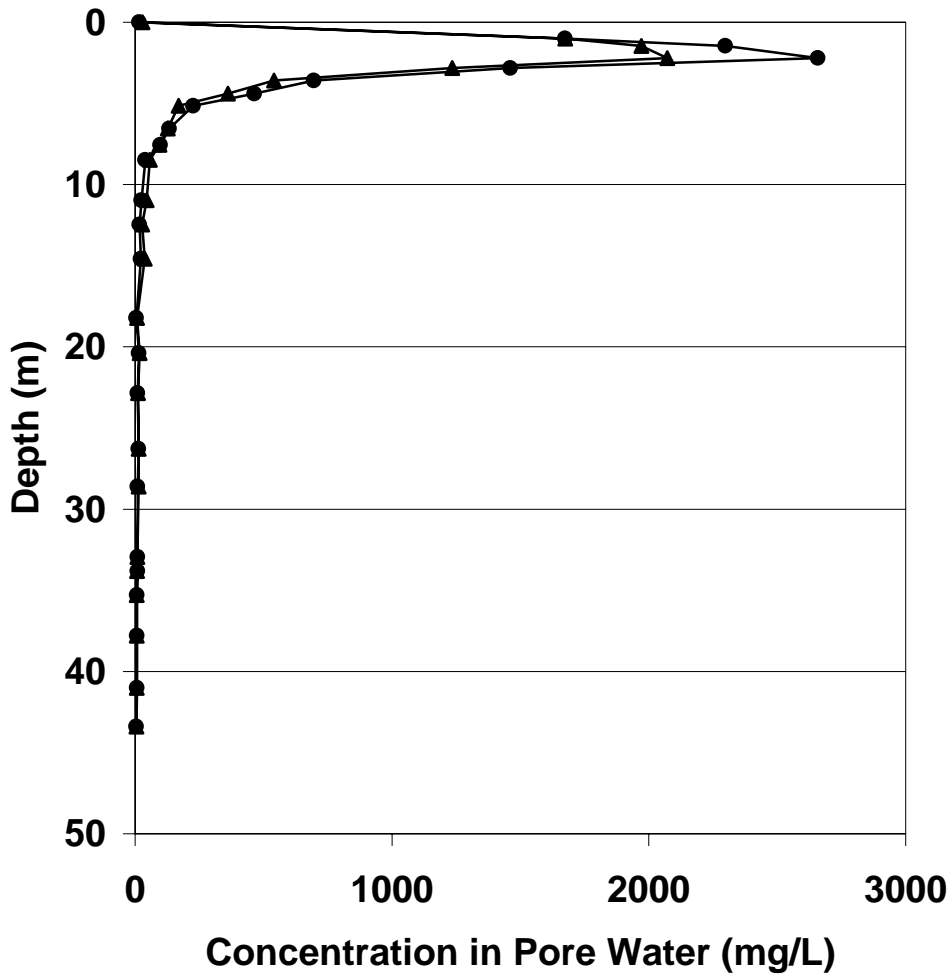


Figure 2a

Chloride (solid triangles) and nitrate (solid circles) concentrations in pore water with depth from the 46 m deep boring. Chloride and nitrogen concentrations in the pore waters were analyzed on 1:1 dilution extracts via HPLC and ion chromatography. The profile shows unexpected nitrate peak that corresponds with the chloride peak beneath the rooting zone. Concentrations are reported as calculated pore water concentrations, corrected for in-situ volumetric water content. All nitrogen in the pore waters were measured and reported as NO₃-N. The low water contents and the oxidizing environment of the near surface discourage the presence of other nitrogen species

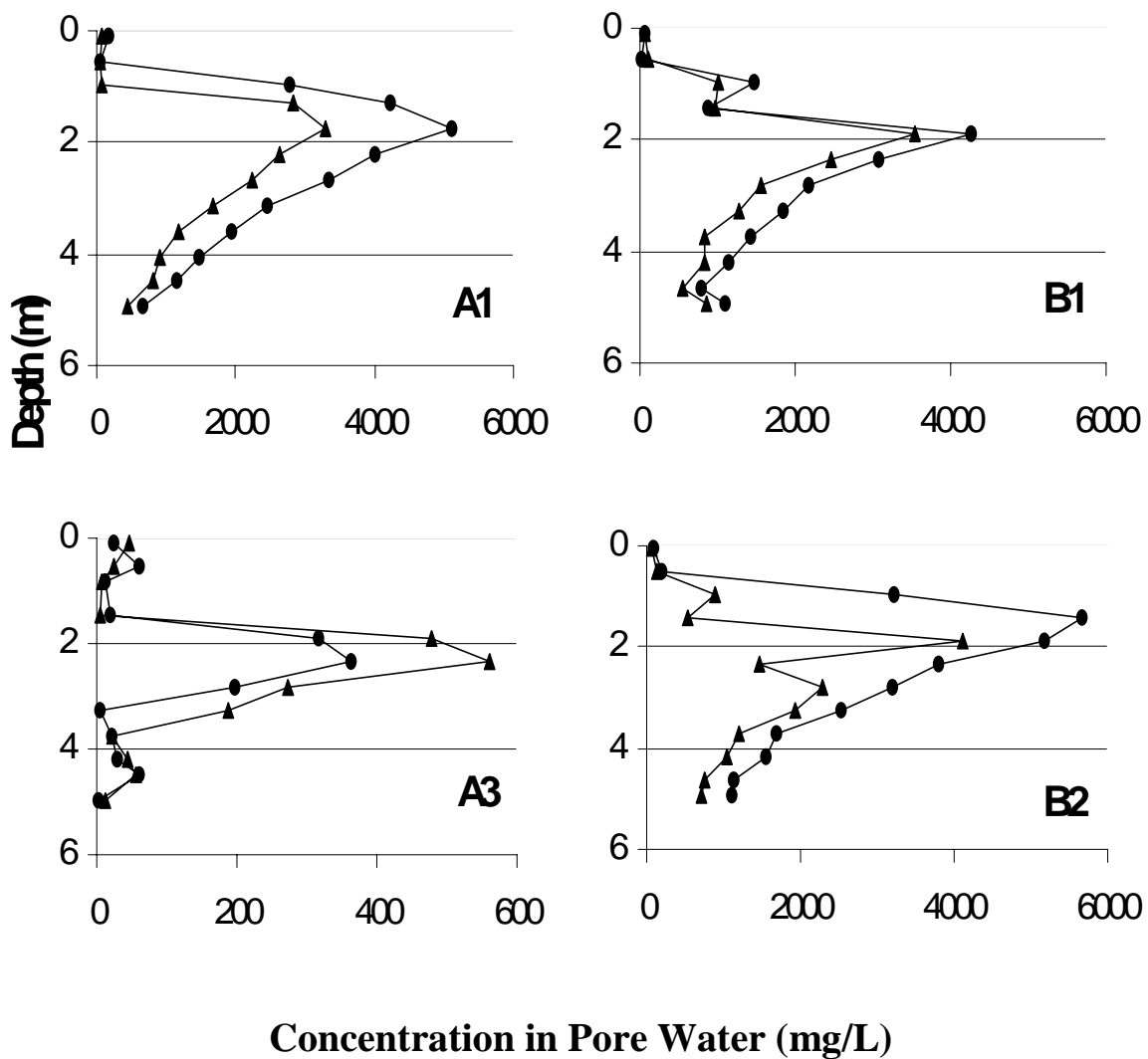


Figure 2b
 Chloride (solid triangles) and nitrate (solid circles) concentrations in pore water with depth from the shallow corings. Nitrate peaks below the root zone track the chloride peaks over several different time scales. The 4 cores shown are representative of the 3 remaining cores not shown. Note that core A3 contains significantly lower concentrations due to its location in a small (<0.5 m) ephemeral channel.

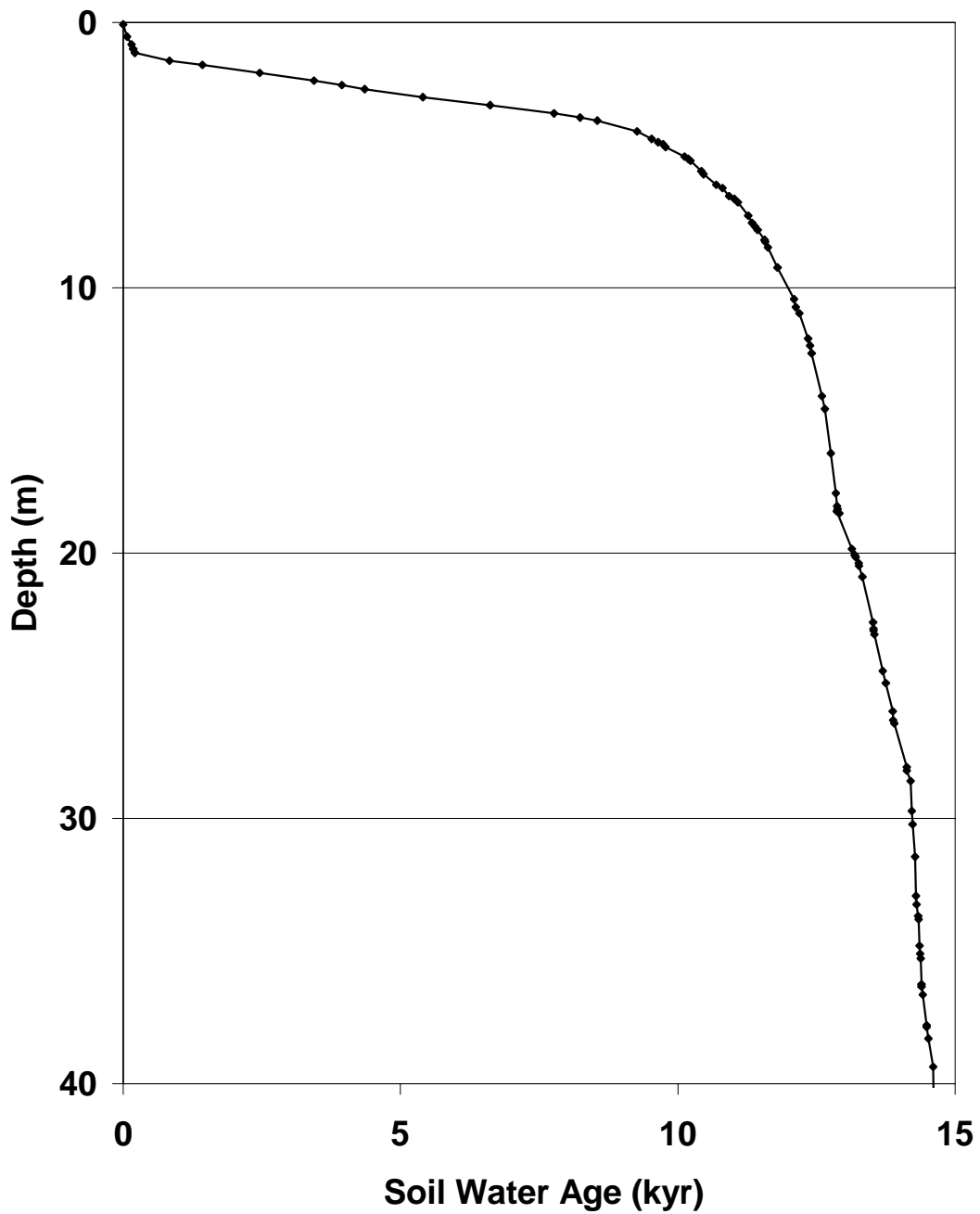


Figure 3a

Soil water age, based on the chloride accumulation, with depth in the 46-m coring. Profile contains a record of accumulation since last period of significant recharge coinciding with the last full glacial maximum. Chloride flux at the land surface was estimated to be $88\text{mg/m}^2/\text{yr}$, similar to modern measured and inferred flux

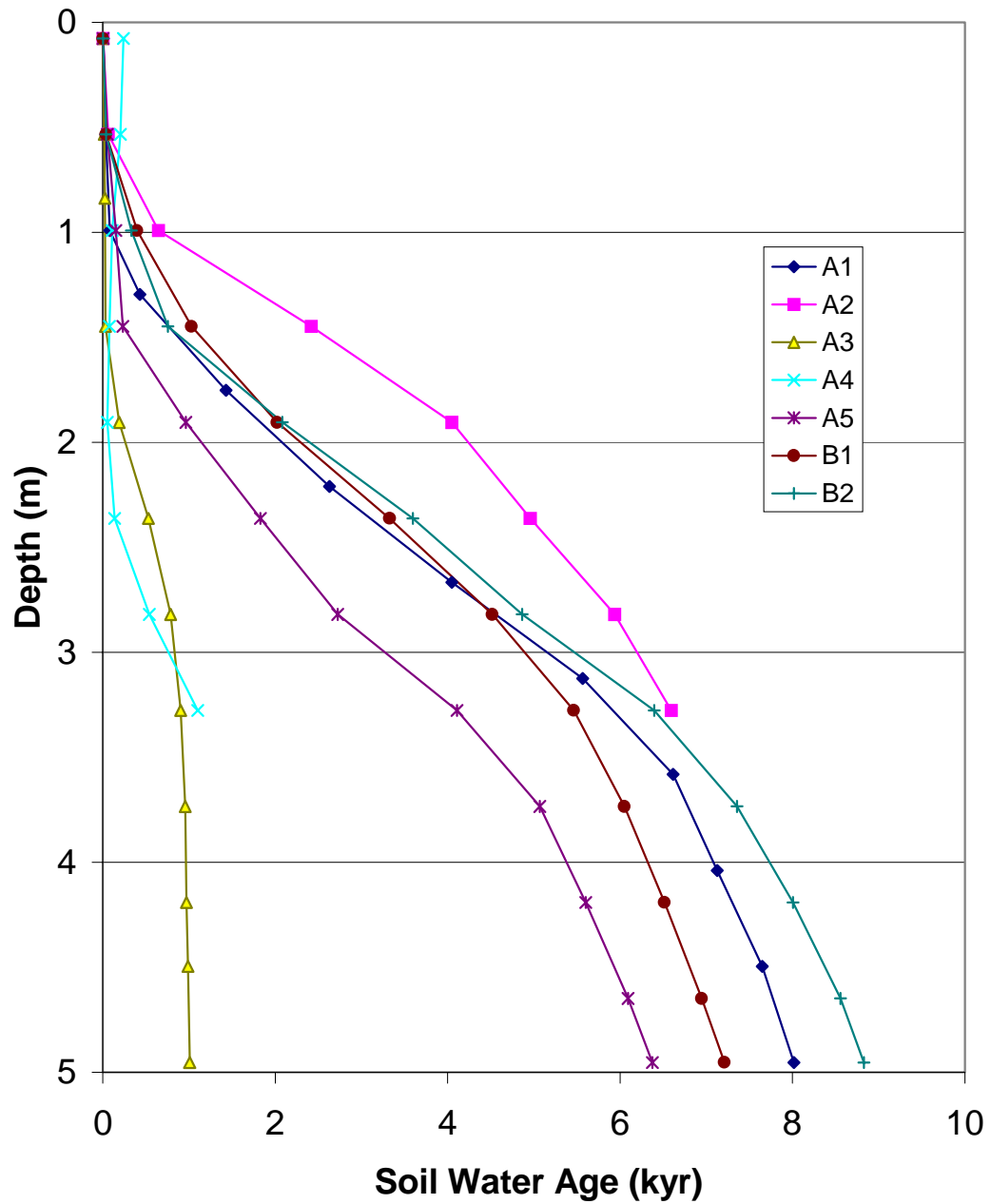


Figure 3b
 Soil water age based on chloride accumulation, with depth in the shallow corings. The spread of ages indicates spatial heterogeneity in recharge over the small area. Cores A3 and A4, which record less than 2000 yr. of accumulated Cl were augured in slight depressions that occasionally contain overland flow.